CARBONYL, HALOACID, HALOACETATE, AND HALOACETAMIDE METHODS

Methods for carbonyl, haloacetate, and haloacetamide target DBPs were developed at the University of North Carolina (UNC). A listing of these DBPs is presented in Table 1. For many of the targeted species, no chemical standards were commercially available. Therefore, synthesis was required for many. Proton nuclear magnetic resonance spectroscopy (NMR) and gas chromatography (GC) with ion trap mass spectrometry (MS) detection were used to confirm the identity and establish purities for these synthesized standards. The standards were stored at –15°C and periodically reassessed for purity. Extraction methods developed included liquid-liquid extraction (LLE) and solid phase extraction (SPE), which were used in combination with different derivatization techniques (e.g., methylation or pentafluorobenzylhydroxylamine [PFBHA] derivatization) and GC with electron capture detection (ECD) or mass spectrometry (MS) (Table 1). Liquid chromatography (LC) with electrospray ionization (ESI)-MS was also investigated for two of the target DBPs, but quantitative methods at the low μg/L detection limits were effected through the use of gas chromatography. The stability of these DBPs in water was also investigated

Table 1. Target carbonyl, haloacid, haloacetate, and haloamide compounds[1]

Compound	Abbreviation	Source of Standard	Purity	Analytical Method
3,3-dichloropropenoic acid	DCPA	Synthesized at UNC	>95% by NMR	LLE – diazomethane
Dimethylglyoxal (2,3-butanedione)	23BD	Aldrich	97%	PFBHA-LLE
Chloroacetaldehyde	CA	ChemService and Aldrich	50% solution in water	PFBHA-LLE
Bromochloroacetaldehyde	BCA	Can Syn	35%	LLE, PFBHA-LLE
Dichloroacetaldehyde	DCA	TCI America	>95% by GC/EI-MS	LLE, PFBHA-LLE
Bromochloromethyl acetate	BCMA	Supelco	>99.99%	LLE
2-Chloroacetamide		Aldrich	98%	LLE
2,2-Dichloroacetamide		Aldrich	98%	LLE
2-Bromoacetamide		Aldrich	98%	LLE
2,2-Dibromoacetamide		Sigma-Aldrich	98%	LLE
2,2,2-Trichloroacetamide		Aldrich	99%	LLE
Trans-2-hexenal	TH	Acros	99%	PFBHA-LLE, SPE-ESI
5-Keto-1-hexanal	5KH	Majestic Research	~20%	PFBHA-LLE, SPE-ESI
Cyanoformaldehyde-oxime	CNF	Can Syn	51%	LLE
6-Hydroxy-2-hexanone	6HH	Majestic Research	>95%	PFBHA-LLE, SPE-ESI

[1]Abbreviations: Can Syn: Synthesized by Can Syn Chem Corp (Toronto, ON, Canada); TCI America (Portland, Ore.); Aldrich Chemical Co. (St. Louis, Mo.); Acros Organics (Pittsburgh, PA); Majestic Research: Synthesized by Majestic Research (Athens, GA).

SAMPLE COLLECTION

Amber glass bottles (20 mL for carbonyl, haloacetate, and haloacetamide samples; 250 mL for haloacid samples) containing a quenching agent and labeled according to sample site and location, quenching agent added, and date were sent in coolers to each drinking water utility for sampling. Samples were collected headspace-free in these vials by staff at the water utilities. Travel blanks were prepared in the same manner, but were pre-filled with deionized water and capped with no headspace. All bottles for the same sample location and site were individually wrapped in bubble wrap and packaged together and labeled with the sample site and location. Bubble-wrapped bottles were then packed into a padded cooler along with a check-list of bottles sent and ice packs. Once samples were collected at the utility, they were shipped back to UNC overnight.

CARBONYL METHOD

Figure 1 provides of summary of the procedure used to quantify the carbonyl DBPs in drinking water samples. Methods published by Yu et al. (1995) and the U.S. EPA (Method 556) served as the basis for the method used here.

Concentrations of stock solutions prepared are summarized in Table 2. Dilutions were made using methanol (Dilution I and II) or deionized water (DIW) (Dilution III). Solutions of the surrogate standard, 4-fluorobenzaldehyde, were made up in methanol, and solutions of the internal standard (IS), 1,2-dibromopropane, were made up in hexane. Dilution III solutions could be used for 2-3 days. PFBHA solutions were prepared fresh for each derivatization/extraction. Stock solutions of all compounds, internal standard and surrogate standard and their dilutions were stored at $4^{o}C$ when not in use. Calibration curves were created using different concentration ranges (in the low μg/L range) for each DBP (Table 3).

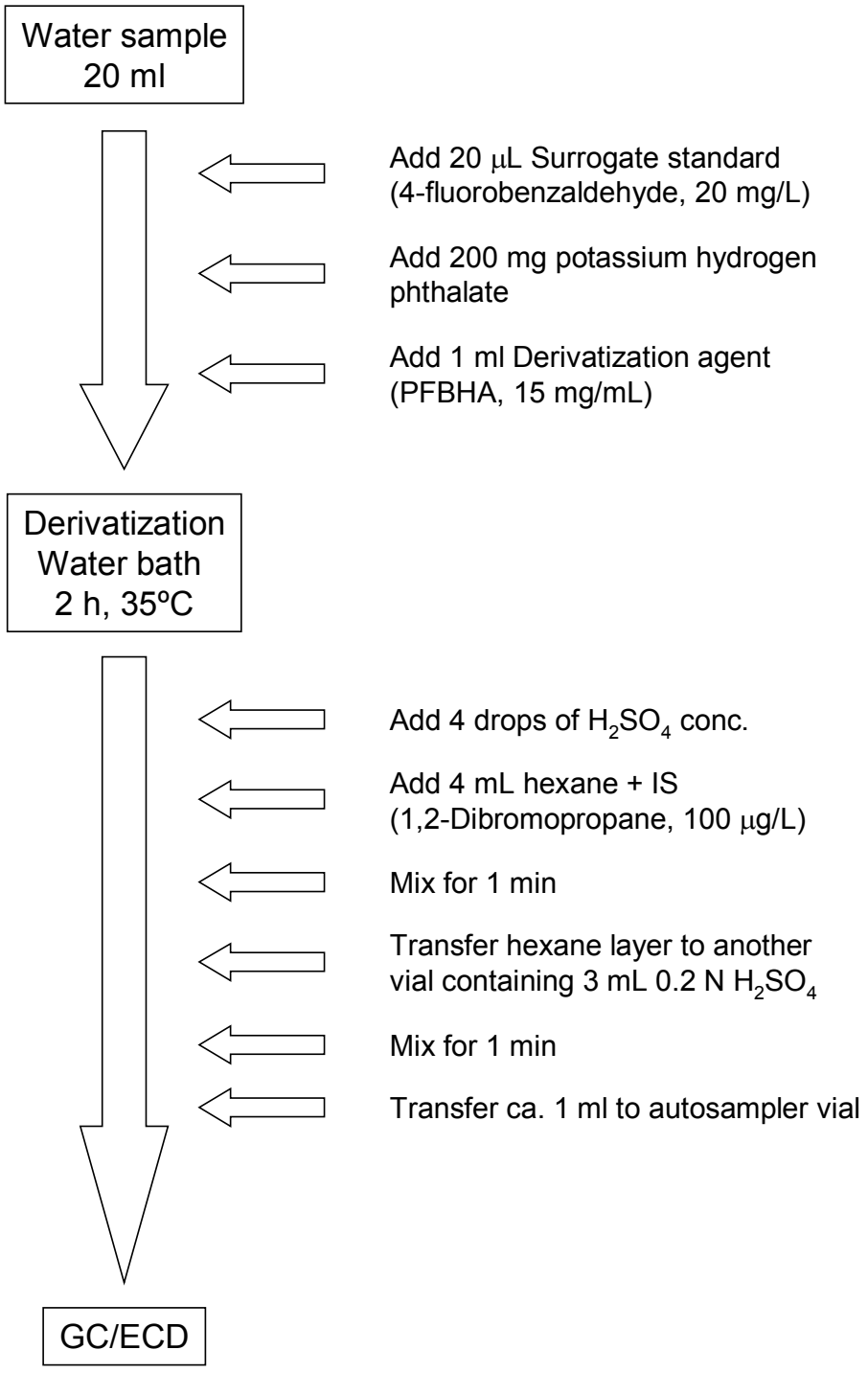


Figure 1. Summary of procedure used to quantify carbonyl DBPs in water.

Table 2. Carbonyl Stock Solutions and Dilutions

Compound	Dilution I [a]	Dilution II [a]	Dilution III
	Conc. (g/L MeOH)	*Conc (mg/L MeOH)*	*Conc ($\mu g/L$ H_2O)*
Chloroacetaldehyde	12.035	120.35	1203.50
Bromochloroacetaldehyde + Dichloroacetaldehyde	0.242 0.345	9.68 13.80	96.80 138.00
Dichloroacetaldehyde	2.156	86.24	862.40
Tribromoacetaldehyde	26.825	10.73	107.30
Trans-2-hexenal	8.3	9.96	99.60
6-Hydroxy-2-hexanone	3.204	51.26	512.60
5-Keto-1-hexanal	1.106	11.06	110.60
2,3-Butandione	10.111	10.11	101.11
Cyanoformaldehyde-oxime	0.956	9.56	95.6
4-Fluorobenzaldehyde (Surrogate Standard)	235.44	23.544	
1,2-Dibromopropane (Internal Standard)	939.85	9.3985	

[a] Solutions of the internal standard were made in hexane

Table 3. Concentrations used for calibration curves (solutions in deionized water)

CA	BCA	DCA	TBA	TH	23BD	5KH	6HH	CNF
1.204	0.097	1.000	0.107	0.100	0.101	0.111	0.513	2.88
2.407	0.194	2.001	0.215	0.199	0.202	0.221	1.025	5.8
6.018	0.484	5.002	0.537	0.498	0.506	0.553	2.563	14.4
12.035	0.968	10.004	1.073	0.996	1.011	1.106	5.126	28.8
24.070	1.936	20.008	2.146	1.992	2.022	2.212	10.252	57.6

Derivatization and Extraction

Briefly, the pentafluorobenzylhydroxylamine (PFBHA) derivatization procedure was carried out as follows. Twenty mL of each drinking water sample was measured and placed into a 40-mL vial (2 vials per sample). Four 20-mL vials of one sample were also collected from each treatment plant to determine recoveries. Twenty mL of each calibration standard was also measured and placed into 40-mL vials (2 vials per sample). Twenty μL of the surrogate solution (23.5 mg/L of 4-fluorobenzaldehyde) was then spiked into each calibration and aqueous sample, and approximately 200 mg of potassium hydrogen phthalate was added to samples for pH adjustment. One mL of freshly prepared PFBHA (15 mg/mL in deionized water) was then added to each sample, and samples were placed in a water bath at 35^{o}C for 2 hours. After cooling to room temperature, 4 drops of concentrated sulfuric acid (approximately 0.05 mL) was added to prevent the extraction of the unreacted PFBHA reagent, and 4 mL of the internal standard solution (9.4 mg/L in hexane) was added and mixed for 1 min using a vortex mixer. The aqueous and hexane layers were allowed to separate, and the hexane layer was transferred to a separate 20-mL vial that contained 3 mL of 0.2 N sulfuric acid, and was mixed for 1 min using a

vortex mixer. Finally, a disposable pipet was used to draw off the hexane layer into a labeled 1.8-mL autosampler vial. Prior to analysis by GC-ECD, samples were stored in the freezer covered with aluminum foil.

GC-ECD Analysis

GC analyses were carried out on a Baity GC-3 gas chromatograph. Injections of 1 μL of each extract were introduced via a splitless injector onto a DB-1 column (30-m, 0.25 mm ID, 0.25 μm film thickness; J&W Scientific/Agilent, Folsom, CA). The GC temperature program consisted of an initial temperature of 50°C, which was held for 1 min, followed by an increase at a rate of 4°C /min to 250°C, followed by an increase at a rate of 3°C /min to 280°C, which was held for 3 min. The injector and the detector were controlled at 150 and 280°C, respectively. Prior to analyzing the real drinking water extracts, the internal standard solution (in hexane) and the pure hexane used to prepare this solution were analyzed as blanks.

Results

The retention times obtained for the carbonyl standards are shown in Table 4. Two isomers were formed for the PFBHA derivatives—*syn* and *anti*. When these isomers separated by GC, both retention times are given below. Figure 2 shows a representative GC chromatogram, which was used for one of the calibration points. Practical quantitation limits obtained using this method are listed in Table 5, along with typical coefficient of variations for triplicate analyses.

Table 4. Retention times for PFBHA-derivatized DBPs

Compound	Abbrev.	Retention time (min)	
		DB-1	HP-5MS
Chloroacetaldehyde	CA	30.39	18.54
Dichloroacetaldehyde	DCA	32.37 32.64	20.55 20.84
Bromochloroacetaldehyde	BCA	35.14 35.50	23.70
Cyanoformaldehyde	CFA	28.23 28.35	17.37
Trans-2-hexanal	TH	37.26 37.46	25.74
6-Hydroxy-2-hexanone	6HH	39.47 39.90	27.77 28.10
5-Keto-1-hexanal	5KH	39.14 39.65	
2,3-Butanedione	23BD	31.57	39.34
4-Fluorobenzaldehyde (Surrogate)	4FBA	41.38 41.69	29.91 30.09
1,2-Dibromopropane (IS)	12DBP	13.44	4.14

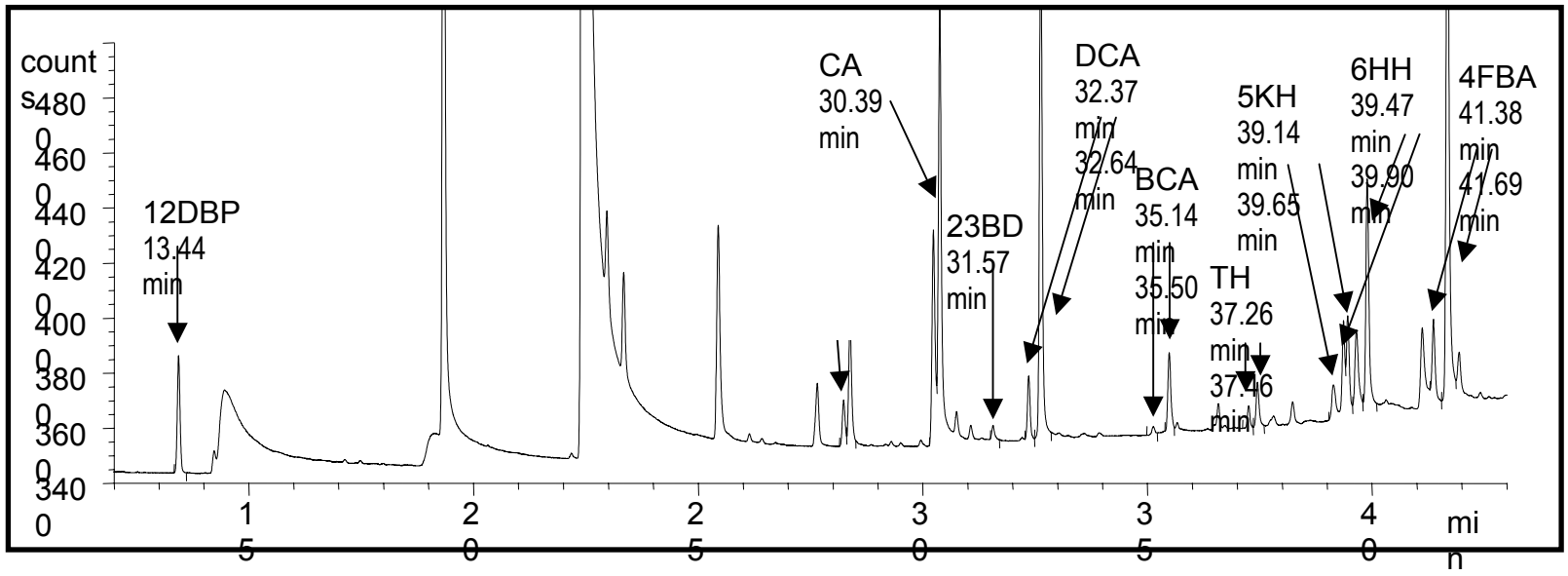


Figure 2. GC-ECD chromatogram showing the different carbonyl-PFBHA derivatives, along with the internal standard (1,2-dibromopropane [2DBP]) and surrogate standard (4-fluorobenzaldehyde [4FBA]). Abbreviations given in Table 1.

Table 5. Practical quantitation limits (PQLs) for carbonyl DBPs

Compound	PQL (μg/L)
Chloroacetaldehyde	0.2
Dichloroacetaldehyde	0.4
Bromochloroacetaldehyde	0.3
Cyanoformaldehyde	3.0
Trans-2-hexanal	0.3
6-Hydroxy-2-hexanone	0.3
5-Keto-1-hexanal	0.8
2,3-Butanedione	0.3

Stability of DBPs

In order to determine an appropriate sample handling procedure, a variety of quenching agents were assessed over a 7-day holding time. Although sodium sulfite appeared to maintain levels of carbonyl DBPs over the 14-day period, it was not chosen as the quenching agent because it is capable of participating in side reactions with other precursors to generate the DBPs studied here. Therefore, for the sake of consistency with other methods used for this study, ammonium sulfate, which also adequately preserved the DBPs over the 14-day period, was selected as the quenching agent for these compounds.

Compound Notes

Haloacetaldehydes. PFBHA derivatization in water generated a consistent 85% conversion of chloro- and dichloroacetaldehyde to the corresponding oximes in a variety of matrices. For the measurement of bromochloroacetaldehyde, dichloroacetaldehyde was found to be a major contaminant in the synthesized product; therefore, the product generated by PFBHA derivatization contained a mixture of 35% bromochloroacetaldehyde and 38% dichloroacetaldehyde. These "standards" were used to quantify the conversion of the aldehyde to the oxime during *in situ* derivatizations in water. Derivatizations showed a consistent 75% conversion. The sum of the *syn* and *anti* isomers used for quantitation of bromochloroacetaldehyde in water.

Cyanoformaldehyde. While the PFBHA oxime standard of this species was synthesized and successfully characterized, many attempts at the synthesis of the target aldehyde were unsuccessful. Consequently, only semi-quantitative analysis of this compound could be made.

Trans-2-hexenal. Both *syn* and *anti* oxime isomers were formed by PFBHA derivatization, and the sum of these peaks was used to quantify *trans*-2-hexenal in water.

6-Hydroxy-2-hexanone. Both *syn* and *anti* oxime isomers were formed by PFBHA derivatization, and the sum of these peaks was used to quantify *trans*-2-hexenal in water.

5-Keto-1-hexanal. Both *syn* and *anti* oxime isomers were formed by PFBHA derivatization, and the sum of these peaks was used to quantify *trans*-2-hexenal in water.

2,3-Butanedione (dimethyl glyoxal). Matrix effects suppressed the ability of the diketone to form a di-derivatized oxime. However, quantitation was possible by calibrating using both the mono- and di-oximes and summing their concentration for the overall concentration of 2,3-butanedione in the original water sample.

3,3-DICHLOROPROPENOIC ACID METHOD

Liquid-liquid extraction (LLE) and diazomethane derivatization were used with GC-ECD detection to quantify 3,3-dichloropropenoic acid (DCPA) in drinking water samples (a modified EPA Method 552 approach). A practical quantitation limit (PQL) of 0.3 μg/L was obtained.

Extraction and Derivatization

Samples were equilibrated to room temperature; two duplicate 20-mL samples were used to analyze for DCPA. Calibration standards were prepared in deionized water at concentrations of 1.9, 4.75, 9.5, 19, and 47.5 μg/L. Twenty mL of each of the two duplicate samples was measured into 40-mL vials, and 50 μL of the surrogate solution (2,3-dibromopropanoic acid, 20 mg/mL) was added to each sample. Concentrated sulfuric acid (1.5 mL) was then added, vials were cooled to room temperature, and 4 mL of the internal standard (100 μg/L in MtBE) was added to each sample. Approximately 6 g of sodium sulfate was added to each vial and was mixed by vortex for at least 1 min. The upper ether layer was then transferred to a 2-mL volumetric flask, magnesium sulfate was added, and flasks were cooled in the refrigerator for 10 min.

Cold diazomethane solution (225 μL, previously prepared according to a slight modification of the method of Glastrup (1998)), was added to each flask and returned to the refrigerator for 30 min. Following this period, flasks were gently removed from the refrigerator and allowed to come to room temperature for 15 min. The presence of a yellow color should remain (indicating the presence of an excess of diazomethane reagent). A small scoop of silicic acid was then added to each sample to quench the excess diazomethane, and 10-15 min was allowed for the solid to settle. The upper ether layer was ten transferred to labeled autosampler vials for GC-ECD analysis. If samples could not be analyzed immediately, autosampler vials containing extracts were stored in the freezer.

GC-ECD Analysis

GC analyses were carried out on a Hewlett-Packard Model 6890 gas chromatograph (Hewlett-Packard/Agilent, Folsom, CA). Injections of 1 μL of each extract were introduced via a splitless injector onto a HP5-MS column (30-m, 0.25 mm ID, 0.25 μm film thickness; J&W Scientific/Agilent, Folsom, CA). The GC temperature program consisted of an initial temperature of 37^{o}C, which was held for 1 min, followed by an increase at a rate of 5^{o}C /min to 280^{o}C, which was held for 30 min. The injector and the detector were controlled at 180 and 297^{o}C, respectively. Prior to analyzing the real drinking water extracts, the internal standard solution (1,2-dibromopropane, 200 mg/L in MtBE) and the pure MtBE used to prepare this

solution were analyzed as blanks, surrogate standards were analyzed for retention time checks, calibration curve samples were analyzed in duplicate, and the internal standard was analyzed once more. Following the analysis of samples (in order of increasing concentration), the internal standard was analyzed again.

Stability

3,3-Dichloropropenoic acid showed good stability in water. Degradation was not detected when ammonium sulfate was used to quench residual chlorine, nor when the aqueous sample was stored for up to 14 days at 14^{o}C.

HALOACETATE METHOD

Bromochloromethylacetate was the only haloacetate DBP targeted in this study. A pure standard was obtained from Supelco and checked for purity using NMR and GC/MS. A liquid-liquid extraction (LLE)-GC-ECD method similar to that of EPA Method 552.2 was used for quantifying bromochloromethylacetate in water, except that hexane was used in place of MtBE as the extraction solvent. LLE with hexane was found to provide a more consistent and higher recovery (92%) than MtBE (75%). No sample pretreatment or derivatization was necessary for this compound. The practical quantitation limit (PQL) for this compound with a 1:5 concentration factor was determined to be 0.3 μg/L.

Extraction

Samples were equilibrated to room temperature; two duplicate 20-mL samples were used to analyze for bromochloromethylacetate in water. Calibration standards were prepared in deionized water at concentrations of 0.3, 1.0, 5.0, 10.0, and 25.0 μg/L generating a calibration curve with a median regression coefficient (r^2) of 0.998. Twenty mL of each of the two duplicate samples was measured into 40-mL vials, 4 mL of the extracting solvent (hexane) and 100 μg/L internal standard (1,2-dibromopropane) dispensed, and approximately 6 g of sodium sulfate added to each vial, which was then capped and mixed by vortex for at least 1 min. The upper organic layer was then transferred to a 1-mL autosampler vial for analysis by GC-ECD. Spike recoveries were assessed on the plant effluent or average distribution system samples through the addition of 5 μg/L of standard. Typical spike recoveries in these samples fell in the range 80-110% for all samples analyzed in this project. For a single set of triplicate, spiked samples, the coefficient of variation was in the range of 6-10%. All plant samples were collected in vials containing ammonium sulfate to quench residual chlorine. During method development it was observed that the presence of a chloramine or chlorine dioxide residual had no effect on the levels of bromochloromethylacetate spiked into plant waters, provided the samples were stored within 24 hours of collection at 4^{o}C and subsequently analyzed within 14 days. Chlorine-quenched samples (with ammonium sulfate) could be held under similar conditions without compromising sample integrity.

Analysis

The GC-ECD conditions were as follows: a 30-m DB-5 column (J&W Scientific/Agilent, Folsom, CA) with dimensions 0.25 mm I.D. and 0.25μm film thickness) was operated under the following oven temperature program: initial temperature of 50 °C held for 1 min, followed by a temperature gradient of 4°C/min to 250°C, which was held for 3 min. The injector was operated in the splitless mode at a temperature of 180°C, while the μECD was held at a temperature of 300°C. The retention time of the target compound under these conditions (and carrier gas flow-rate of 1 mL/min) was 6.1 min and was well resolved from other co-extracted neutral DBPs, such as trihalomethanes.

HALOACETAMIDE METHODS

The haloacetamides included in this study are listed in Table 6. Several approaches were attempted for these compounds including silylation, a novel liquid chromatography (LC)/MS method, a method involving the conversion of haloacetamides to their corresponding haloacetic acids by acid-catalyzed hydrolysis, and a direct liquid-liquid extraction-GC-ECD method. The silylation method, as described in a paper by Le Lacheur et al. (1993) resulted in a practical quantitation limit of 10 μg/L. The novel LC/MS method in conjunction with solid-phase extraction also showed relatively high detection limits (>20 μg/L). The hydrolysis approach appeared to be the most promising method when initially tested on standards in deionized water, but when tested using real drinking water samples containing natural organic matter, it resulted in the formation of additional halogenated by-products. Finally, a direct LLE with gas chromatography (GC)-electron capture detection (ECD) proved to be the best method to use for quantifying the haloacetamide DBPs for this Nationwide Occurrence Study.

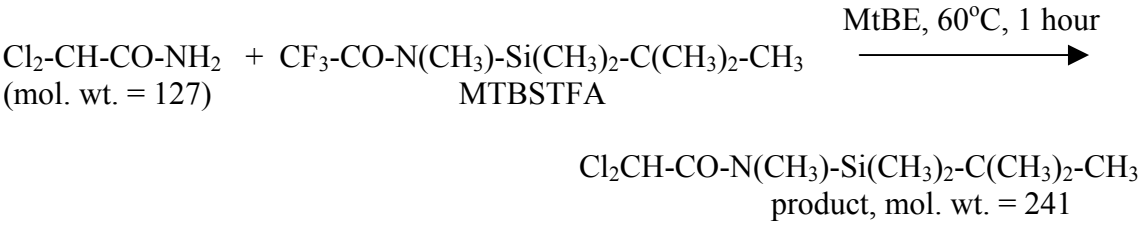
Table 6. Listing of haloacetamides included in this study

Compound	Supplier & cat. #	Final conc. of stock solution (g/L)	Retention Time By GC-ECD
Trichloroacetamide	Aldrich	0.98	25.821
Dibromoacetamide	SALOR(Aldrich)	1.08	27.226
Dichloroacetamide	Aldrich	1.01	21.799
Monobromoacetamide	Aldrich	1.02	22.84
Monochloroacetamide	Aldrich	0.98	17.55

Silylation Method

This method was initially tested using one of the halacetamides--dichloroacetamide. Three dichloroacetamide/MtBE solutions were used: 108, 54 and 1.08 mg/L. One mL of each solution was treated with 100 μL of N-methyl-N-(*tert*-butyldimethylsilyl)trifluoroacetamide (MTBSTFA) and sonicated at 60°C for 1 hour. The solution was then cooled to room

temperature and stored at -20°C until analyzed by GC-ECD using a DB-5 column (J&W Scientific/Agilent, Folsom, CA). The reaction is shown below.



Silyl derivatives were made at four different concentrations of dichloroacetamide in MtBE for use as standards. In a typical experiment, a known amount of dichloroacetamide in 2 mL MtBE was measured into a 4-mL vial. Then, 100 µL of the silylating agent MTBSTFA was injected and the vial kept at 45°C for 2 hours. After cooling, the sample was analyzed by GC-ECD and GC/MS using a 30-m, 0.25 mm, 0.25 µm DB-5 column (J&W Scientific/Agilent, Folsom, CA). The operating conditions were as follows: carrier gas flow rate was 1.2 mL/min, initial oven temperature 50°C for 1 min then 4°C/min to 250°C; with ECD, the splitless mode injector temperature was 180°C and detector temperature was 300°C; with ion trap MS, initial injector temperature was 50°C for 1 min then rapid increase to 250°C. The trap manifold was set at 180°C and transfer line at 280°C. Emission current was 10 µA, mass scan range was from 50-650 Da, and electron multiplier voltage was 1500 V.

The silyl-dichloroacetamide derivative eluted at approximately 15.5 min by GC/MS. Figures 3 shows the electron ionizaton (EI) mass spectrum for the silyl-dichoroacetamide derivative.

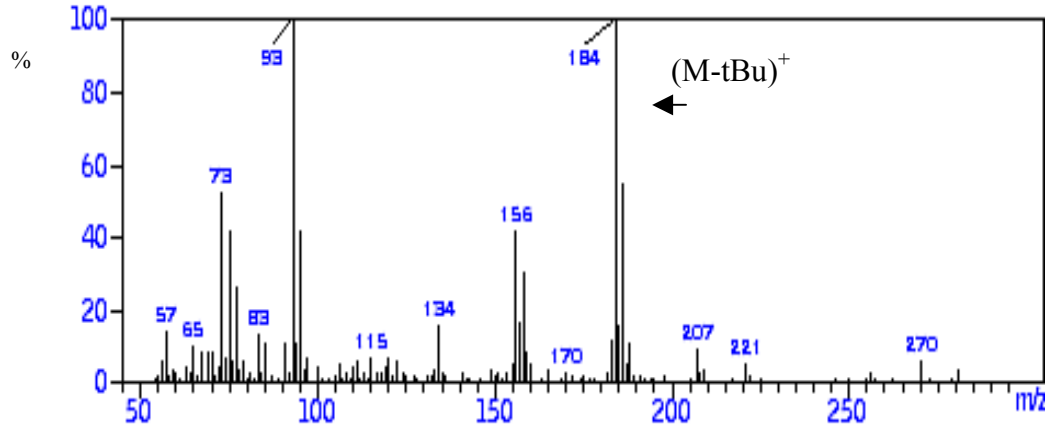


Figure 3. EI mass spectrum of silyl-dichloroacetamide.

Recovery of Dichloroacetamide from Deionized Water. Six concentrations of dichloroacetamide in deionized warer were used. Ten mL of each solution was saturated with sodium sulfate in a 40-mL vial. Five mL of MtBE containing 100pg/μL dibromopropane (internal standard) was added and shaken well to extract the dichloroacetamide. The ether layer was transferred to another vial and dried over anhydrous magnesium sulfate thoroughly before silylation. MTBSTFA (100μL) was injected into each of the vials and kept at 50°C for 1 hour. The solution was then cooled to room temperature and transferred to a GC vial for analysis. The recoveries compared to the standards were very low (4-20%) and suggested that, at least without additional preconcentration, the application of this method for the analysis of dichloroacetamide in water would be limited to a practical quantitation limit of 10μg/L.

Because the recoveries were poor with this method, direct determination of dichloroacetamide from water by solid phase extraction was also attempted, but was not successful.

Acid-Catalyzed Hydrolysis Method

Another method investigated was the acid-catalyzed hydrolysis method. This method involves the acid-catalyzed hydrolysis of the haloacetamide to the corresponding haloacetic acid, as shown below for dichloroacetamide:

$$CHCl_2CONH_2 + H_2O \rightarrow CHCl_2COOH + NH_3$$

The accepted method (EPA Method 552) for haloacetic acids could then be applied before and after hydrolysis to determine the amount of this compound accounted for by the haloacetamide.

For the analysis of the haloacetic acids (EPA Method 552), an aqueous sample was treated with concentrated sulfuric acid, saturated with salt, extracted with MtBE and methylated with diazomethane and determined as its ester. Assuming that the low molecular weight amide may undergo acid-catalyzed hydrolysis readily with concentrated sulfuric acid and the heat generated during the addition, this assumption was tested by making fairly concentrated solutions of dichloroacetamide in deionized water and subjecting to the procedure for the analysis of dichloroacetic acid. This procedure produced a recovery of 38 % for dichloroacetamide.

In order to optimize the method, experiments were carried out to determine the effect of different acid concentrations on the degree of dichloroacetamide hydrolysis. The following scenarios were investigated on a 20 mL aqueous sample for a 2 hour reaction: at ambient temperature (23^{o}C), no acid was compared to the addition of 4 mL sulfuric acid; at a water bath temperature of 80^{o}C, no acid was compared to 4 and 6 mL of sulfuric acid. A 200 μg/L solution of dichloroacetamide was used, and if the conversion were 100 %, 201.5 μg/L of dichloracetic acid would be generated. Results shown in Table 7 reveal an optimum conversion with the addition of 4 mL sulfuric acid at 80^{o}C.

Using the 80°C – 4 mL acid scenario, tests were then made to determine whether the reaction time could be reduced without significantly impacting recovery. The results are shown in Table 8.

Table 7. Impact of different reaction conditions on the hydrolysis of dichloroacetamide to dichloroacetic acid (DCAA)

Sample	DCAA measured (μg/L)	% Conversion
Ambient no acid	23.31	11.57
Ambient – 4 mL acid	151.2	75.04
80°C – no acid	115.3	57.22
80°C – 4 mL acid	**195.7**	**97.12**
80°C – 6 mL acid	146.0	72.46

Table 8. Impact of different reaction times on the hydrolysis of dichloroacetamide to dichloroacetic acid (DCAA) using 4 mL acid at 80°C

Reaction time (hours)	DCAA measured (μg/L)	% Conversion
0	55.4	27.49
0.5	175.9	87.30
1	**183.4**	**91.02**
2	184.4	91.51
3	179.4	89.03
4	177.5	88.09

It was apparent that a 1 hour reaction would suffice. Using this optimized set of reaction conditions, dichloroacetamide solutions in a concentration range from 0 to 200 μg/L were taken through the hydrolysis process and the resultant equivalent amount of DCAA calculated. A plot of these values shown in Figure 4 indicates an average 82% conversion using a linear regression.

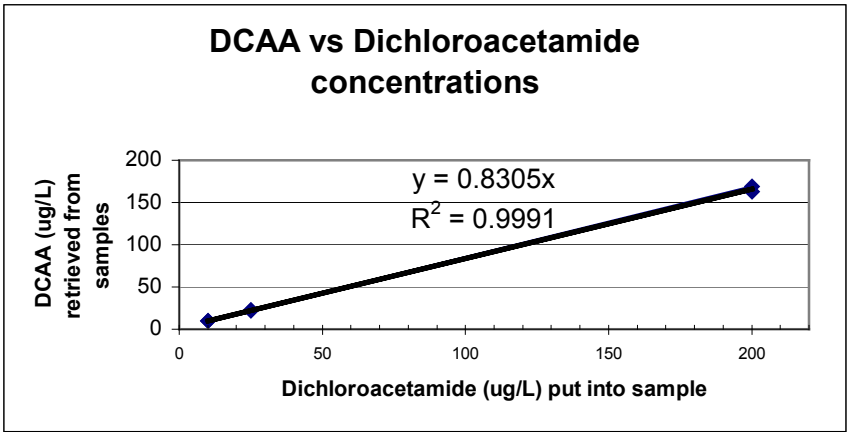


Figure 4. Formation of DCAA from dichloroacetamide over a wide concentration range.

LLE-GC-ECD Method

A final method, involving a simple liquid-liquid extraction (LLE) and GC-ECD analysis proved to be the best method to use for this study. A 100 mL aliquot of 200 μg/L dichloroacetamide in deionized water was prepared by diluting 1 mL of 20 mg/L dichloroacetamide in MtBE to a final volume of 100 mL with deionized water. Four 20 mL aliquots were measured into clean 20 mL vials with Teflon-lined screw caps. Four mL of MtBE and the internal standard (100 μg/L of 2,3 dibromopropane in MtBE) were added to two of the aliquots, while 4 mL of ethyl acetate (EtAC) was added to the two remaining aliquots. Each vial was vortexed for 1 min and the solvent layer allowed to separate for five min. The extracts were compared to a standard of dichloracetamide at the 100% recovery level of 1 mg/L. A 1-mL sample of the organic layer was then analyzed by GC-ECD under the following conditions:

GC Column: 30-m, 0.25 mm ID, 0.25 μm film thickness HP5-MS (Hewlett-Packard/Agilent, Folsom, CA); oven temperature program - initial temperature: 37°C, held for 1 min; 5°C/min increase to 280°C. The injector and detector temperatures were 180 and 300°C, respectively, and the injector was operated in the splitless mode. The recoveries of each sample are shown in Table 9.

Table 9. Recovery of dichloroacetamide by liquid-liquid extraction from deionized water

Sample	Extraction solvent	Retention time (min)	Peak area	Expected peak area	Recovery (%)
1	MtBE	10.521	7737.71	33255	23.27
2	MtBE	10.521	7509.28	33255	22.58
3	EtAC	10.550	19798	33255	59.53
4	EtAC	10.552	19163.5	33255	57.63

Based on the percent recoveries, ethyl acetate appeared to be a better solvent for extracting dichloroacetamide from water. This approach was then expanded for the other haloacetamides listed in Table 6. The statistical evaluation of this method is presented in Table 10. The linear calibration range extended from 1 to 50 μg/L, and water samples were spiked at 5 μg/L.

Table 10. Statistical evaluation of LLE method for haloacetamides in water

Compound	PQL (μg/L)	Average % CV at 1 μg/L	Average Spike Recovery (%)
Trichloroacetamide	0.1	8.4	95
Dibromoacetamide	0.1	6.5	90
Dichloroacetamide	0.1	5.4	104
Monobromoacetamide	0.1	10.3	88
Monochloroacetamide	0.1	11.3	78

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